

COMMUNICATION

Synthesis and electronic structure of the first cyaphide-alkynyl complexes[†]

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The novel complexes *trans*-[Ru(dppe)₂(C≡CR)(C≡P)] (R = CO₂Me, C₆H₄OMe), the first to incorporate cyaphide as part of a conjugated system, are obtained in facile manner. The electronic structure of these compounds is probed by X-ray, DFT and UV/Vis studies.

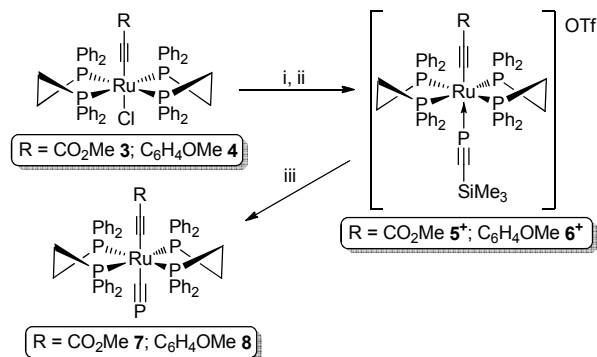
Low coordinate phosphacarbons (e.g. RC≡P, R₂C=PR') have long been a source of intrigue,¹ being isolobal and isoelectronic analogues of more familiar carbo-centric and nitrogenous species, yet still embodying appreciable dichotomies. For instance, the chemistry of phosphalkynes and phosphalkenes is dominated by the high-energy π-systems (HOMO) akin to classical alkynes and alkenes, yet the lone pairs remain accessible (*cf.* nitriles and imines) to engage in reactivity,² albeit that those of phosphalkynes are appreciably stabilised. Such varied facets render low-coordinate phosphacarbons attractive moieties to incorporate into electro-active and conducting molecules as a means of moderating orbital distributions and energies, and thus the molecular electronic properties. Indeed, this is illustrated by numerous examples³ of phosphalkene⁴ and phosphole-based⁵ systems, which exhibit enhanced electrochemical and photo-electronic responses in comparison to carbo-centric and nitrogen-doped analogues.

In respect of phosphalkynes, however, such application has yet to be realised, a direct corollary of a lack of intrinsic kinetic stability within the C≡P moiety and resulting difficulties in accessing appropriate derivatives. Indeed, even complexes of the notionally simple cyaphide ligand (C≡P[−]), a direct analogue of the ubiquitous cyanide, have long evaded isolation.⁶ Though first observed by Angelici in 1992, in the complex “Cl(Et₃P)₂Pt(C≡P)”,⁷ later trapped as [Cl(Et₃P)₂Pt(μ-η¹-η²-C≡P)Pt(PEt₃)₂],^{7,8} only in 2006 was Grützmacher able to isolate the first unequivocal example of a terminal cyaphide complex, *viz.* [RuH(dppe)₂(C≡P)] (1),⁹ obtained from the η¹-phosphalkyne complex [RuH(dppe)₂(P≡CSiPh₃)]⁺ (2⁺) by base-induced desilylative rearrangement.^{9,10} Since this seminal report, no further examples have been described, though Russell and co-workers recently inferred the *in situ* formation of *trans*-[Mo(dppe)₂(C≡P)(P≡CSiMe₃)][−],¹¹ albeit unisolated.

We are interested in the chemical and electronic properties of organometallics that comprise low-coordinate phosphacarbons,¹²

particularly those involving metal-centred conjugation. To this end, Grützmacher's methodology presented an intriguing opportunity. Herein, we report the synthesis and isolation of the first compounds to incorporate the cyaphide ligand as part of an extended π-system; we also outline preliminary investigations into the electronic structure of these molecules.

The ruthenium alkynyl complexes [Ru(dppe)₂(C≡CR)Cl] (R = CO₂Me **3**,¹³ *p*-C₆H₄OMe **4**) were converted *in situ* to the respective triflate salts by reaction with AgOTf, subsequent treatment with Me₃SiC≡P affording [Ru(dppe)₂(η¹-P≡CSiMe₃)(C≡CR)]⁺ (R = CO₂Me **5**⁺, *p*-C₆H₄OMe **6**⁺) in good yields (Scheme 1).



Scheme 1. Reagents and conditions: (i) AgOTf, CH₂Cl₂; (ii) P≡CSiMe₃, CH₂Cl₂/C₇H₇; (iii) KO^tBu, thf.

The identities of **5**⁺ and **6**⁺ follow convincingly from multinuclear NMR spectroscopic data. Thus, the ³¹P{¹H} NMR spectra exhibit quintet and doublet resonances (**5**⁺: δ_p 108.6; **6**⁺: δ_p 113.1) in 1:4 ratio, with mutual couplings of ca 30 Hz. A singlet resonance corresponding to the SiMe₃ group is apparent in the ¹H NMR spectra, in each case integrating consistently with the dppe backbone, and exhibiting correlation (HMBC) with a characteristic doublet in the ¹³C{¹H} NMR spectra (δ_c ~ 190) attributed to the phosphalkynic centre, and thus confirming the P≡CSiMe₃ moiety. Retention of the alkynyl functionality is similarly confirmed, as is the presence of triflate (δ_F −78.9), while bulk purity was established by microanalysis. The spectroscopic data resemble those reported

for **2**⁺, differences in chemical shift being attributable to a more electron withdrawing nature for the metal fragments of **5**⁺ and **6**⁺, and thus differing polarization of the alkyne P and C centres.

The molecular connectivity was further supported by isolation of X-ray quality crystals of **5.OTf**, obtained by slow cooling of a saturated CDCl₃ solution of the salt (Figure 1).¹⁴ The cation exhibits the anticipated geometry, with the trans-disposed alkynyl and phosphalkyne adopting near perfect linearity ($\angle\text{C-Ru-P}$ 177.0(3), $\angle\text{Ru-C}\equiv\text{C}$ 178.0(10); $\angle\text{Ru-P}\equiv\text{C}$ 175.7(4) °); this contrasts the situation observed in **2**⁺ and Jones' [RuH(dppe)₂(η^1 -P \equiv CMe)],¹⁵ both of which exhibit appreciably bent geometries for the phosphalkyne unit ($\angle\text{Ru-P}\equiv\text{C}$ 165.5(2)⁸ and 153.7(2) ° respectively), attributed to steric encumbrance. The internal geometry of **5**⁺ is largely unremarkable; the C \equiv P linkage (1.528(11) Å) is comparable to those of **2**⁺ (1.530(3) Å)⁹ and Russell's *trans*-[Mo(dppe)₂(η^1 -P \equiv CSiMe₃)₂] (1.540(2) Å),¹¹ which are consistent with prior examples.^{15,16} A somewhat short C \equiv C distance is noted, (1.153(15) Å; cf. 1.16 – 2.25 Å from a CCDC search¹⁷), but is mirrored in the parent alkynyl **3** (1.136(10) Å), and presumably results from disorder within this unit.

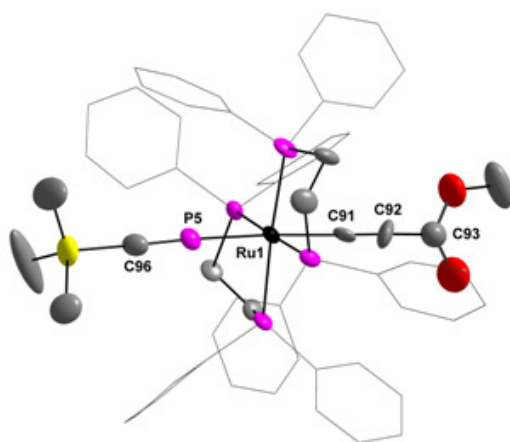


Figure 1. Molecular structure of **5**⁺ in crystals of **5.OTf**, DCM solvate. Hydrogen atoms are omitted and phenyl rings reduced for clarity; 50 % thermal ellipsoids. Selected Bond distances (Å) and angles (deg): Ru(1)-C(91) 2.082(11), C(96)-P(5) 1.528(11), C(96)-Si(1) 1.858(12), C(91)-C(92) 1.153(15), C(92)-C(93) 1.450, P(5)-C(96)-Si(1) 178.3(6), C(95)-P(5)-Ru(1) 175.7(4), P(5)-Ru(1)-C(91) 177.0(3), C(96)-C(92)-C(93) 171.9(12)

Treatment of **5**⁺ or **6**⁺ with a single equivalent of KO^tBu in thf solution effects desilylative rearrangement to afford the cyaphide complexes **7** and **8** respectively, isolated in excess of 60 % yield. Notably, this reaction proceeds to completion within 1 h. under ambient conditions; this contrasts the case of **1**, for which extended reaction times (14 h.) were required. Moreover, while Grützmacher observed a kinetically-favoured “intermediate” (believed to be [Ru(dppe)₂{C(SiPh₃)=P(OPh)}] (**A**), formed by reversible attack of [−]OPh at phosphorus), no comparable species are apparent in the formation of **7** or **8**. Indeed, even *in situ* NMR studies at −78 °C failed to reveal any intermediates, or significantly slow the reaction. Since **A** was not considered to lie on the pathway leading to cyaphide,¹⁰ we reason that the faster reactions can be attributed to its absence, which is presumably the result of diminished electrophilicity at phosphorus in **5**⁺ / **6**⁺, combined with enhanced facility of direct nucleophilic attack at the smaller SiMe₃ (cf. SiPh₃).

Formation of the cyaphide complexes is convincingly established from spectroscopic data, supported in the case of **8** by an X-ray diffraction study (Figure 2).¹⁸ Spectroscopically, a significant shift to higher-frequency is noted for both alkyne and dppe phosphorus centres (**7**: δ_P 161.5, 52.7; **8**: δ_P 159.5, 50.8) when compared to **5**⁺

and **6**⁺, with concomitant reduction in the mutual spin-spin coupling constant (to ~ 4 Hz), consistent with increased separation of the interacting nuclei (*i.e.* $^3J_{PP}$ vs $^2J_{PP}$). A significant shift is also noted for the phosphalkynic carbon centre ($\Delta\delta_C$ ~86), similar to that observed by Grützmacher. The ¹H and ¹³C{¹H} spectra confirm loss of the SiMe₃ group and retention of the respective alkynyl ligands, which is further supported by infrared data (**7**: ν_{CO} 1660 cm^{−1} ν_{CC} 2040 cm^{−1}; **8**: ν_{CC} 2032 cm^{−1}); the C \equiv P stretching mode is also observed in both infrared and Raman spectra (**7**: 1255 cm^{−1}; **8**: 1261 cm^{−1}) and is in good agreement with that reported for **1** (1239 cm^{−1}) and those calculated for **7** and **8** (~1240 cm^{−1}; see ESI).

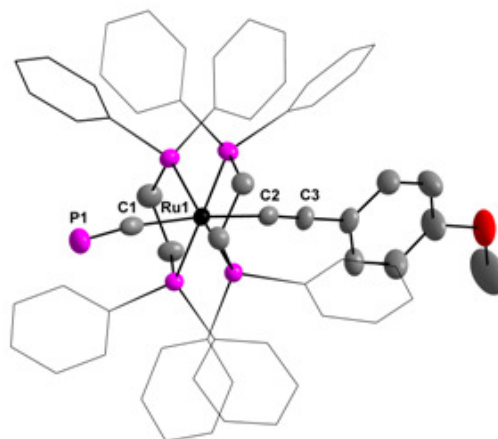


Figure 2. Molecular structure of **8**. Hydrogen atoms omitted and phenyl rings reduced for clarity; 50 % thermal ellipsoids. Selected bond distances (Å) and angles (deg.): C(1)-P(1) 1.544(4), Ru(1)-C(1) 2.065(4), Ru(1)-C(2) 2.084(3), C(2)-C(3) 1.205(5), Ru(1)-C(1)-P(1) 172.3(2), Ru(1)-C(2)-C(3) 174.4(3), C(1)-Ru(1)-C(2) 171.91(14), C(2)-C(3)-C(4) 178.5(4).

In the solid state, **8** exhibits slight distortion from linearity ($\angle\text{Ru-C}\equiv\text{C}$ 174.4(3) °; $\angle\text{Ru-C}\equiv\text{P}$ 172.3(2) °), as previously noted for other *trans*-bisalkynyls.¹⁹ A shorter C \equiv P (1.544(4) Å) and very slightly longer Ru–CP (2.065(4) Å) bond are noted as compared with **1** (1.573(2) and 2.057(2) Å respectively), presumably reflecting diminished $d_{\pi} \rightarrow \pi^*_{(C\equiv P)}$ retrodonation within **8**, due to the competing *trans*-alkynyl. It is, however, noteworthy that DFT studies[§] indicate greater linearity within the conjugated system of **8**, together with a longer C \equiv P linkage (1.58 Å), a situation that is mirrored for **7**; this would perhaps imply incidence of packing effects in the solid state.

The frontier orbitals of **7** and **8** (Figure 3) are similar to those typically seen in alkynyl and bis(alkynyl) complexes.²⁰ Thus, the HOMO and HOMO-1 in each case derive from the out-of-phase mixing of the Ru (d_{xy} , d_{xz}), C \equiv C (π) and C \equiv P (π) orbitals, with an appreciable contribution from the cyaphide moiety. This is most pronounced for **7** (50 % $\pi_{(C\equiv P)}$, 35 % Ru) in which the electron-withdrawing methylpropiolate ligand contributes only ca 10% to either orbital. In contrast, the more donating C \equiv CC₆H₄OMe ligand contributes significantly to the HOMO of **8** (24 % $\pi_{C\equiv C}$, 17 % π_{Ar} cf. 30 % Ru, 24 % $\pi_{C\equiv P}$), leading to reduced involvement of the cyaphide, which in turn dominates the orthogonally-lying HOMO-1 (43 % $\pi_{C\equiv P}$, 35 % Ru, 14 % $\pi_{C\equiv C}$), lying 0.2 eV lower in energy (cf. 0.01 eV for **7**). The LUMO of each molecule is appreciably separated from the HOMO (ΔE 3.45 eV **7**, 3.7 eV **8**) and centred on the dppe ligands (ca 75 %) and Ru $d_{x^2-y^2}$ orbital (25 %), with appreciable Ru–P antibonding character. Higher energy orbitals (up to LUMO+10) are almost exclusively ligand (dppe) based, while the C \equiv P π^* orbitals do not contribute appreciably until LUMO+18/19; the C \equiv C (and for **8** Ar) π^* orbitals feature from LUMO+11.

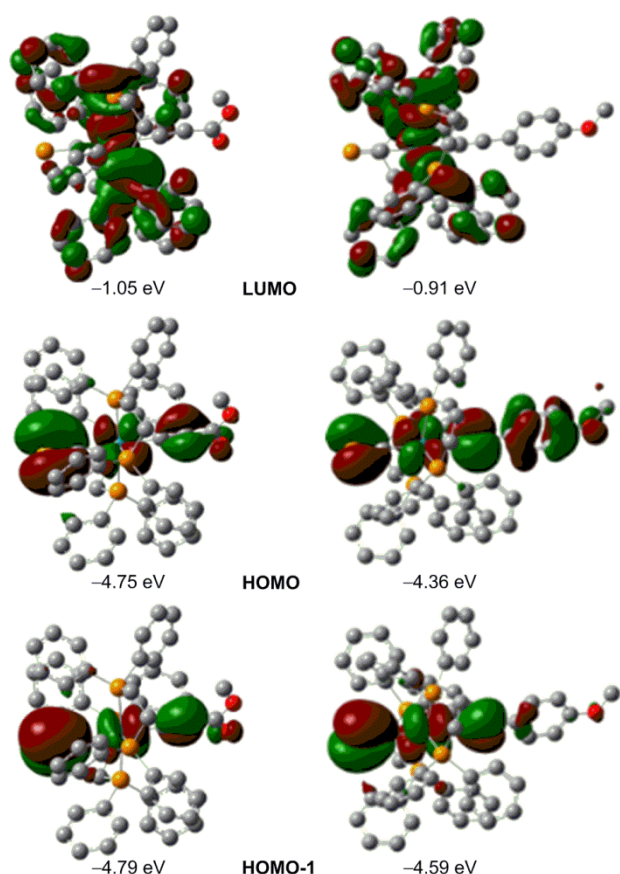


Figure 3. Frontier Molecular Orbitals for **7** (left) and **8** (right).

It is noteworthy that the lone-pair of the cyaphide moiety is appreciably stabilised with respect to the π -system, lying ca 1.6 eV below the HOMO (HOMO-6 in **7**, HOMO-7 in **8**). In each case, NBO calculations reveal the lone-pair to be held in an orbital of ca 75 % *s* and 25 % *p* character, with polarisation of the C \equiv P moiety in the sense P δ^+ –C δ^- . In this regard, the cyaphide closely resembles classical phosphalkynes.

Both **7** and **8** were further studied by a combination of UV/Vis spectroscopy and TD-DFT (calculating the first 100 excited states; see ESI for details). Both exhibit strong absorptions around 250 nm (40000 cm $^{-1}$) arising from Ligand \rightarrow Ligand charge transfer (LLCT) between the π -CP/CC and dppe π^* orbitals. For **7**, a further feature around 275 nm (36363 cm $^{-1}$) is again dominated by LLCT transitions but also involves some Intraligand transitions (ILCT) centred on $\pi_{\text{C}\equiv\text{P}} \rightarrow \pi^*_{\text{C}\equiv\text{P}}$. A weaker feature around 300 nm (33333 cm $^{-1}$) is again dominated by LLCT. In contrast, while a dominance of LLCT is also apparent for **8**, a strong feature around 298 nm (33550 cm $^{-1}$) involves significant contributions from ILCT, centred on $\pi \rightarrow \pi^*$ transitions of the alkynyl (HOMO \rightarrow LUMO+11) and C \equiv P (HOMO \rightarrow LUMO+18/19) ligands; a smaller contribution from metal \rightarrow ligand charge transfer (MLCT) is evident between ruthenium and the dppe π^* orbitals (HOMO \rightarrow LUMO+5, 9, 10).

In conclusion, we have described the first organometallic complexes to incorporate the terminal cyaphide ligand as part of an extended π -system; this also represents only the second unequivocal report of a terminal metal-cyaphide complex. Structural and theoretical studies reveal a modestly screened cyaphide moiety with a stabilised, but nonetheless accessible, lone-pair akin to classical phosphalkynes. The cyaphide contributes significantly to the

HOMO and HOMO-1, with an influence that is clearly moderated by the trans-alkynyl ligand. The molecules absorb strongly in the UV region, their electronic spectra being dominated by LLCT transitions to the dppe ligands, though ILCT $\pi \rightarrow \pi^*$ transitions within the C \equiv P moiety also contribute, most significantly so in **8** for which further ILCT occurs within the C \equiv CC $_6$ H $_4$ OMe ligand. These molecules are the first of a novel class of conjugated, organometallic hetero-ynyl complexes that we continue to explore and develop.

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Notes and references

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†Electronic Supplementary Information (ESI) available: Full synthetic details and characterising data for all compounds, computational details, UV/Vis data, CCDC 962350, 962351, 990881 (in CIF format) and ellipsoid plot of **3**. See DOI: 10.1039/c000000x/

‡ The novel complex **3** was prepared by a modification of established synthetic routes to ruthenium alkynyl complexes. See ESI for full details and characterising data.¹³

§ Calculations used the B3LYP hybrid-functional, with the lanl2dz basis set for Ru and 6-31G** for all other atoms; see ESI for full details.

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